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ON THE CORROSION OF POWDER COPPER

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Copper powders have found wide application in ^{many} branches of industry, yet their resistance to corrosion is quite low. Frequently copper powder in an air-tight container is delivered to the consumer in an oxidized state. There are cases of corrosion during the manufacturing process of powders.

Despite numerous items of literature on the problems of atmospheric corrosion of copper, there are no investigations on the corrosion of copper powders. Meanwhile, there is no doubt that the corrosion of powder copper must have a specific character, different from corrosion of the compact metal. This character is conditioned by the presence of an enormously developed surface of highly-dispersed copper. If, for example, a copper cube of one cubic cm in volume is crushed till its particles pass through a 325-mesh sieve (44 microns), the surface of the particles will amount to 384,000 sq cm; i.e. the surface of the same quantity of copper will grow 64,000 times from the original 6 sq cm surface of the cube. Surface activity increases accordingly. Actually, the real surface of the powder is still larger, taking into consideration the dendritic form of its grains.

It has been found [1], that a liquid film 10^{-4} mm thick is formed on a smooth surface of metal in open air at 20°C and 50% humidity. Only upon heating the metal to 30°C does this water film disappear. It is natural to suppose that for powder copper, possessing a much greater force of surface adsorption, the phenomena of capillary condensation and the formation of a continuous thin water-film, enveloping the grains of powder, are absolutely inevitable. The formation and presence of such a film may take place long before the above-mentioned humidity is reached, and at temperatures probably considerably higher than 30°C.

The presence of a liquid film on the surface of the powder grains is, seemingly, an imperative condition for development of the corrosive process.

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Taking into consideration the obscurity of the subjects, here brought to attention, and under the necessity of establishing methods for the stabilization of powder, it would be interesting to study the oxidation rates of powder in the air, the effect of temperature, moisture and various gases in the atmosphere on corrosion, and the action of certain other reagents.

EXPERIMENTAL PART

Since the corrosion products of copper powder (salts or oxides of copper) are usually nonvolatile, the gravimetric method was used for corrosion tests, conducted basically with industrial copper powder 99.56% pure with weight equal to 1.58 g/cu cm.

To determine the oxidation extent of copper powder in respect to storage time, tests were conducted in a laboratory atmosphere for 80 days. 2.5-3 g of powder were placed on watch-glasses 40 mm in diameter, covered with funnels for dust protection, and kept on laboratory tables. The average data of at least two parallel experiments are presented in Table 1.

Table 1.

Oxidation Rate of Copper Powder Under Laboratory Conditions at $16 \pm 2^\circ\text{C}$

	Keeping Time (days)				
	1	10	30	60	80
Weight of powder (in g)	2.8280	5.7661	5.9066	5.4820	5.4820
Increase in weight (in g)	0.0006	0.0027	0.0044	0.0155	0.0213
Relative increase in weight (%)	0.02	0.04	0.14	0.28	0.38

Table 1 shows that the monthly increase in weight of the powder is equal to 0.14%, which rate corresponds to oxidation of 0.12% of powder per month in conversion of corrosion products to Cu_2O .

To investigate the temperature effect, experiments were performed in 6-liter copper bombs, hermetically sealed and placed into an oil thermostat with automatic regulator which permitted temperature control accurate to $\pm 3^\circ\text{C}$.

The copper bombs were first cleaned with benzene and sulfuric ether. Samples of powder in similar glass beakers were placed inside the bombs, and time was registered from the moment when the required temperature was reached. Upon completion of the tests, the samples were transferred into desiccators with calcium chloride, cooled to room temperature and weighed. Two parallel experiments were run in each case. Changes in the amount of moisture were observed simultaneously with changes in temperature. Test results are given in Table 2.

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Table 2.

Effect of Temperature and Moisture on Corrosion of Copper Powder During a 24-Hour Period. (Increase in weight is expressed in % of initial weight)

Conditions of experiment	Temperature			
	20°C	40°C	60°C	75°C
In the air at atmospheric pressure	0.02	0.035	0.032	0.057
Air saturated with water vapor at atmospheric pressure	0.03	0.11	0.49	0.54

Results of this series of experiments show that the rate of atmospheric corrosion of copper powders increases continuously as the temperature rises and has no maximum in the temperature range studied thus far. This factor indicates extraordinary stability of the water films enveloping the powder grains, whereas similar films on smooth metallic surfaces, as was noted above [1], entirely disappear on heating to 30°C.

To clarify the effect of moisture on the corrosion of copper powder at constant temperature, additional experiments were conducted. The results are presented in Table 3 and Figure 1.

Table 3

Effect of Moisture on Corrosion of Powder Copper at $16 \pm 2^\circ\text{C}$

Conditions of experiment	Keeping time (days)				
	1	7	10	30	60
In laboratory atmosphere	0.02	-	0.04	0.14	0.28
In desiccator with H_2SO_4 (Sp. g 1.84)	0.02	-	-	0.017	0.012
In desiccator with CaCl_2	-	-0.024	-	-	-
In sealed vessel in air saturated with water vapor	0.08	0.28	0.41	-	-

The numerical data in Table 3 express relative increase in weight in percentage of initial weight. As is shown, copper powder placed in a desiccator, practically was not oxidized during 2 months, while the powder sample, kept in the laboratory atmosphere for the same period, increased its weight by 0.3%; and powder in the vapor-saturated atmosphere reached this value of corrosion after one week.

Analysis of powder, kept in the desiccator with freshly prepared calcium chloride, showed that there was no color change which would indicate any degree of oxidation. Decrease in its weight by 0.024% occurred due to the absorption of moisture, contained in the copper powder, by calcium chloride.

Effect of gases and other reagents:

Corrosion tests of powder copper were conducted in atmospheres of ammonia, hydrogen chloride, sulfur dioxide and carbon dioxide. Gases were first purified

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and then dried with sulfuric acid. Parallel experiments were staged in atmospheres of the pure gases contained in a space saturated with water vapor.

In the case of studying the effect of ammonia, a tray with a 25% aqueous solution was placed into the reaction space. Porcelain beakers 55 mm high and 29 mm in diameter, containing 2-2.5 g of powder were installed into 2-liter glass jars, sealed after installation with paraffin to secure airtightness. Filling of jars with gas was checked each time. After completing the experiment, beakers were transferred to a desiccator and, upon attaining constant weight, the increase in weight was determined. Results of tests are given in Table 4 and graphically represented in Figure 2. Data on the corrosion of powder in the air are also presented to compare the corrosive effects of the various gases.

Analysis of results obtained permits the following conclusions: In the first place, activity of hydrogen chloride not saturated with water vapors is very high; and the value characterizing corrosion in an atmosphere of dry hydrogen chloride passes through a maximum, whereas in the atmosphere of hydrogen chloride saturated with water vapors, this value increases continuously; secondly, corrosive activity of all other gases is sharply increased if water vapors are present at the same time.

Table 4

Effect of Various Gases on Corrosion of Powder Copper at Temperature of $16 \pm 2^\circ\text{C}$. (Increase in weight is expressed in % of initial weight)

Atmospheric Conditions										
Time (hr)	Air	Air, saturated with water vapor	CO ₂	CO ₂ , saturated with water vapor	SO ₂	SO ₂ , saturated with water vapor	NH ₃	NH ₃ , saturated with water vapor	HCl	HCl, saturated with water vapor
24	0.02	0.03	0.002	0.72	0.26	5.55	0.57	3.86	6.0	2.46
48		0.11	0.1	3.04	0.40	10.06	0.67	5.06	26.32	5.63
240	0.04	0.41	0.28	10.9	0.72	21.9	0.8	8.84	11.03	9.33

It was also revealed (Table 5) that the corrosion resistance of the powder depends on the extent of its initial oxidation.

Table 5

Effect of the Degree of Corrosion of Copper Powder on its Corrosion in Dry Hydrogen Chloride. (Time: 48 hr; temperature: $16 \pm 2^\circ\text{C}$)

Kind of Powder	Copper Content (in %) Before Experiment	Increase in Weight (in %)
Powder Prepared in Laboratory	99.79	29.2
Commercial Powder	98.9	39.9
Oxidized Powder	96.1	51.1

In all experiments, moisture was observed on the walls of porcelain beakers and glass jars, particularly, an increased amount during experiments with the oxidized powder.

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Experiments were also conducted to study the influence of certain ammonium salts on the corrosion of copper powder in cases where they are stored near each other. Samples of powder in porcelain beakers were placed, as in other experiments, inside of glass jars; but other beakers in the same jar contained a certain ammonium salt and water. Jars were hermetically sealed for the duration of the experiment.

Especially noticeable is the extent of corrosion in the presence of ammonium carbonate and particularly in the presence of ammonium carbonate and water (Table 6).

Table 6

Corrosion of Copper Powder When Kept Together with Ammonium Salts
(Time: 264 hr., Temperature: $16 \pm 2^\circ\text{C}$)

Conditions of Experiments	Increase in Weight (%)
1 In the Presence of Ammonium Chloride	0.06
2 In the Presence of Ammonium Chloride and Water	0.20
3 In the Presence of Ammonium Carbonate	11.35
4 In the Presence of Ammonium Carbonate and Water	32.6

Results of the corrosion tests conducted show that powder copper is subject predominantly to electrochemical corrosion under normal temperature conditions in atmospheres of the reagents tested up to this time.

The corrosion mechanism may be represented in the following way. Gases, present in the atmosphere, are adsorbed and dissolved in a thin film of water which covers the surface of the metal grains. Since the solubility of certain gases is very high (for example, one volume of water dissolves 400 volumes of hydrogen chloride), electrolytes of considerably high concentrations may be created in the liquid film even with a low content of gases in the air.

A similar situation will be observed in the case when the powder is washed in sufficiently and the bath electrolyte, being dissolved in the water film, also forms an aggressive corrosive medium.

Thus, moisture appears to be the first and basic factor conditioning corrosion in powder copper. Introduction of dry gases into the reaction space actually only created the conditions necessary for the appearance of a liquid aggressive medium on the surface of the powder grains.

Thickness of the liquid surface film increased with an increase in the concentration of water vapor in the atmosphere of gases being tested. Consequently, the electrical conductivity of the film also increased.

Thus, the presence of an aggressive reagent which, being dissolved in the liquid adsorption film creates an aggressive medium -- an electrolyte -- is a second factor conditioning the corrosion of copper powder.

Finally, corrosion of copper in nonoxidizing media proceeds with the participation of oxygen [2] which, reacting with the copper, forms oxides better soluble in an aggressive medium than pure copper, or gives soluble products of corrosion.

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At a certain ratio between the pH values and concentration of copper ions in solution, oxygen apparently serves as the depolarizer of the cathode process. Oxygen is inevitably present in copper powder in a free state as an air component and also in the form of copper oxides [3] which are formed during electrolysis [4].

Thus, oxygen is the third factor which creates conditions for corrosion of the powder.

The physically-nonuniform dendritic structure of the surface of the powder grains contributes to the origin of its electrochemical heterogeneity, i.e. promotes development of the difference of potentials on various portions of the surface.

The anomalous behavior of dry hydrogen chloride may be explained by the formation of the corrosion products in the form of complex copper compounds. It is known that the reaction of chloride solutions with copper may produce such complex compounds as $3\text{CuO} \cdot \text{CuCl}_2 \cdot 3\text{H}_2\text{O}$, $\text{Cu}(\text{OH})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ and others [2]. Introducing dry hydrogen chloride into the reaction space and having only 0.02-0.03 % of residual moisture in the powder, we create, in the liquid surface film, a concentration of HCl considerably greater than that in the case when the reaction space is filled with hydrogen chloride and saturated water vapor.

According to investigations by Akimov and Rosenfeld [2], the corrosion rate sharply increases in the acid region of chloride solutions. This is caused by the more positive potential of the cathode sections. Hydrochloric acid is consumed in the course of the corrosive process and, since its further replacement is limited, the pH value of the film is on the increase, thus eliminating conditions for promoting the formation of new complex compounds. This leads to a decrease in the corrosion rate and to transformation of the earlier-formed complex products into other simpler ones.

Consequently, a decrease in weight of the corrosion products causes a maximum on the "corrosion-time" curve [Figure 2]. Contrary to this case, high concentration of HCl in the liquid surface film is not created by filling the reaction space with hydrogen chloride and water vapors, and therefore there are no conditions favorable to the formation of complex copper compounds. The process proceeds more slowly without a maximum bend on the "corrosion-time" curve.

To corroborate the mechanism of the anomalous effect of dry hydrogen chloride, additional corrosion tests were conducted to determine the copper content in corrosion products which were separated from noncorroded copper by treatment in a 5% solution of sulfuric acid at 20°C with correction for a blank test.

Table 7

Copper Content in Corrosion Products of Powder Copper in an Atmosphere of Dry Hydrogen Chloride at $16 \pm 2^\circ\text{C}$.

Copper Content in Powder (in %)	Time (hr)	Copper Content (in %)		Ratio of Corroded Copper to Total Amount
		In Products of Corrosion	In Noncorroded Portion	
98.9	24	11.2	87.5	11.3
98.9	48	14.2	84.7	14.4
98.9	240	22.3	76.5	22.5

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Table 9

Influence of Corrosive Volume on the Corrosion Extent of Powder Copper in an Atmosphere of Dry Hydrogen. (Time: 48 hr., Temperature: $16 \pm 2^\circ\text{C}$)

Sample Weight (in grams)	Corrosive Volume (in liters)	Weight Increase (in %)
2.96	1.16	38.1
3.1	6	89.5

Conclusions

1. Corrosion tests of powder copper were conducted at various temperatures in atmospheres of ammonia, hydrogen chloride, carbon dioxide and sulfur dioxide. It was shown, that moisture is a basic factor in the corrosive process in powders. In all cases the temperature coefficient of the corrosion rate (from 0 to 75°C) has a positive value.

2. The anomalous corrosive behavior of hydrogen chloride, compared with other gases, was revealed; and an explanation of this anomaly is given.

3. Corrosion tests of powder copper were conducted in the presence of ammonium salts. It was shown that the presence of moisture promotes decomposition of ammonium salts and, consequently, accelerates the corrosion of powder copper.

4. The corrosive mechanism of copper powders was interpreted as an electro-chemical process.

Engineer V. I. Kalitova participated in the experimental part of this investigation.

BIBLIOGRAPHY

1. Taedt, Z. Elektrochem., 44, 578 (1938).
2. G. V. Akimov. Osnovy ucheniya o korrozii i zashchite metallov. Metallurgizdat, 1. VII (1946).
3. Faerster und Seidel, Z. Anorg. Chem., 14, 106 (1897).
4. O. Kudra, K. Ivanov, Zh F Kh, VI, 6, 647, 822 (1935); A. I. Levin, ZhFKh, XIX, 8, 780-793 (1946); A. I. Levin, Sbornik trudov VII, No 24, Gidro-metallurgiya medi, nikelya i kobalta, 125-150 (1947).

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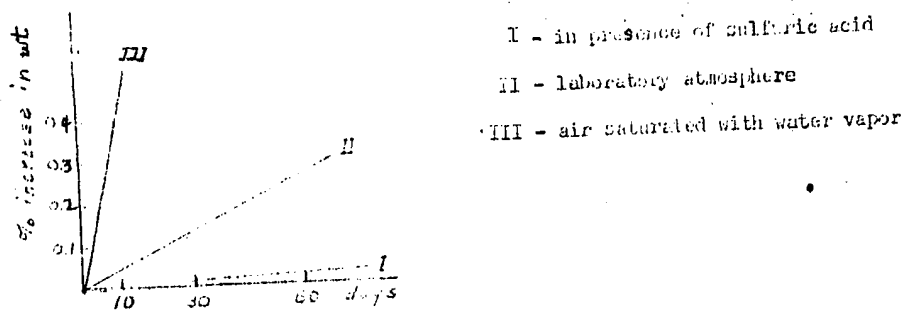


Figure 1. Effect of Moisture on Corrosion of Copper Powder at $16 \pm 2^\circ\text{C}$

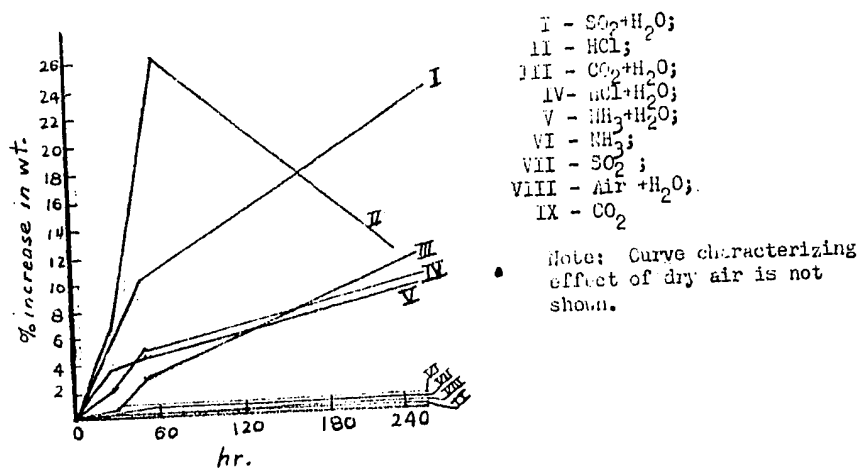


Figure 2. Effect of Various Reagents-gases-on Corrosion of Copper Powder

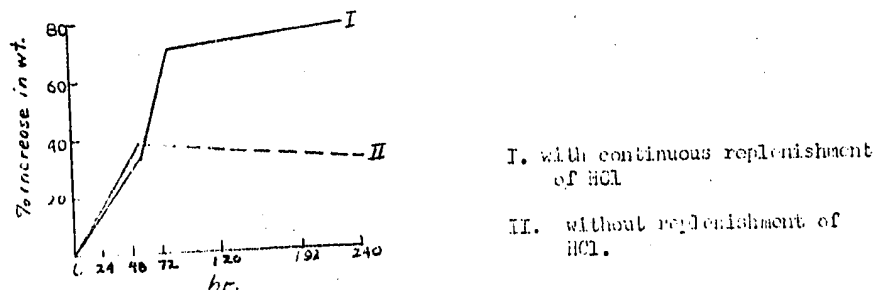


Figure 3. Corrosion of Copper Powder in Dry Hydrogen Chloride

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